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(71) Applicants
S.A.E.I. Celtite,
8 Boulevard Carnot,
Dijon,
Cote D'Or,
France.
Societe D'Etude Et De
Construction De
Machines Pour Toutes
Industries Secoma,
Avenue De Lattre de
Tassigny,
Zone Industrielle,
Meyzieu,
Rhone,
France.
(72) Inventors
Alain Benichou,
Raymond Jean Perraud.
(74) Agents
Messrs J.A. Kemp & Co.,
14 South Square,
Gray's Inn,
London, WC1R 5EU.

(54) **Improvements in compositions and processes for sealing strengthening rods in mines and analogous works**

(57) Resinous compositions of the "single-component" type comprise as fillers, carbon black, 40 to 70% of chalk, and 10 to 40% of quartz sand, and sufficient of a resinous binder comprising unsaturated polyester resin, catalyst and inhibitor to form a matrix for the said fillers, the said percentages being by weight based on the weight of the composition. The carbon black makes it possible to achieve a much better compromise between the viscosity of the composition and its reactivity. Such compositions are useful for positioning strengthening rods in mine levels and other works by introducing into a long bore made in a wall or other surface to be strengthened the composition and a rod of substantially the same length as the bore, and rotating the rod at a rotation speed which causes it to heat up by friction with the composition to the hardening temperature of the composition so as to cause the rod to be sealed in the bore by the hardening of the composition.

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SPECIFICATION

Improvements in compositions and processes for sealing strengthening rods in mines and analogous works

In our British Application No. 44234/78 we have described a process for positioning strengthening rods, which comprise introducing into a long bore, made in a wall or other surface to be strengthened, a thermosetting resinous composition and a metal rod of substantially the same length as the bore, and rotating the rod at a rotation speed which causes it to heat up by friction with the composition to the hardening temperature of the composition so as to cause the rod to be sealed in the bore by the hardening of the composition.

The said Application also describes resin compositions of the "single-component" type which are suitable for use in this process. The Application describes, in particular, three formulations each consisting of a resinous matrix (consisting of an unsaturated polyester resin, a colloidal silica, a catalyst, such as, for example, tert.-butyl perbenzoate, and an inhibitor, such as, for example, 2,6-di-tert.-butyl-para-cresol), chalk and quartz sand. In these three formulations, the percentage by weight of the matrix is respectively equal to 20.31 %, 19.05 % and 17.74 %, which leads respectively to viscosities at 20°C of 870, 1,000 and 1,300 poises. Thus the percentages of resinous binder indicated in the said Application, lead to mastics possessing a relatively high viscosity. This results in two disadvantages and one advantage. The first disadvantage is that certain difficulties are encountered in introducing the composition, either in the packaging of the sealing charges or by loose injection, *in situ*, into the bolt holes. The second disadvantage lies in the fact that, in order to introduce the rod to be sealed, with or without simultaneous rotation, it is necessary to use relatively large thrusts. The advantage lies in the fact that a relatively high viscosity accentuates the heating effect during the rotation of the rod, and consequently accelerates the solidification of the mastic and the blocking of the rod. Attempts have therefore been made to achieve a better compromise on the basis of a lower viscosity for an approximately equivalent reactivity of the mastic, without detracting from the stability of the charge.

It has now, surprisingly, been discovered that the incorporation of a certain amount of carbon black into the composition makes it possible to achieve this result.

The present invention accordingly provides resinous compositions of the single component type comprising, as fillers, carbon black, 40 to 70% of chalk, and 10 to 40% of quartz sand, and sufficient of a resinous binder comprising unsaturated polyester resin, catalyst and inhibitor to form a matrix for the said fillers, the said percentages being by weight of the composition.

The carbon black used in the invention may be, for example, pulverulent carbon or carbon in the form of beads, pulverulent carbon being preferred, and especially a carbon black having a BET specific surface area of 30 to 250 m^2/g, preferably about 30 m^2/g. The average size of the carbon particles is preferably 13 to 51 nanometres and especially about 51 nanometres. The proportion of the carbon black is generally 0.5 to 5% by weight based on the weight of the unsaturated polyester resin, the preferred proportion being about 2.15%.

These new compositons may be used in the same way as that described in our aforesaid Application No. 44234/78. The invention therefore includes within its scope a process for positioning a strengthening rod in mine levels and other works which comprises introducing into a long bore made in a wall or other surface to be strengthened a resinous composition as aforesaid and a rod of substantially the same length as the bore and rotating the rod at a rotation speed which causes it to heat up by friction with the composition to the hardening temperature of the composition so as to cause the rod to be sealed in the bore by the hardening of the composition.

The speed of rotation of the rod in this process is normally between 500 and 3000 revolutions per minute and the rod may be introduced into the bore while it is rotating or before it is made to rotate. It is often convenient to operate the process in four successive stages, as follows:

a first stage, in which the resinous composition is injected into the bore so as to fill 35% to 45% of the latter; a second stage, in which the rod which is to be sealed is introduced into the partially filled bore so that about 50% of its length is wetted by the resin; a third stage in which the rod is rotated at 800 to 2400 revolutions per minute for 15 to 60 seconds; and a fourth stage in which the rod is completely driven into the bottom of the hole while the rotation is continued until the resin has completely polymerized.

The following Examples illustrate the invention.

Example 1

A sealing charge of the single-component type, having the following formulation, is prepared:

Unsaturated polyester resin	500 g (25%)
1,1-Di-tert.-butylcyclohexane peroxide (catalyst)	10 g
3,5-Di-tert.-butyl-4-hydroxyanisole (inhibitor)	0.10 g
Carbon black (specific surface area: 30 m^2/g; average particle size: 51nm)	10.75 g
Chalk (for example GY 100 chalk)	1,183 g
Quartz sand (for example 16.14.2 quartz sand)	296 g

Examples of unsaturated polyester resins which can be used are the resins marketed under the trademarks:

Ukapon 77064, Ukapon T 120 SI (Ugine-Kuhlmann) and

Norsodyne 904, 905 and 907 (CDF-CHIMIE)

An equivalent amount of tert.-butyl peroctoate can also be used as the catalyst (or hardener).

Using this composition, a bolting experiment having the following characteristics is carried out:

the diameter of the bore hole is 22 mm;

the length of the metal rod is 1 m;

the diameter of the metal rod is 18 mm; and

the rotation speed of the rod is 1,600 rpm.

Under these conditions, the blocking time for the rod (or hardening time for the composition) is 38 seconds.

Under identical conditions using formulation 1 described in our Application No. 44234/78, (containing approximately 20.31% of binder), a blocking time of 30 seconds was obtained. Thus, the presence of carbon black has made it possible to obtain an equivalent blocking time for a higher proportion of binder (25% instead of about 20%).

Example 2

A second sealing charge according to the present invention, having the following formulation, is prepared:

Unsaturated polyester resin	500 g (25%)
1,1-Di-tert.-butylcyclohexane peroxide (catalyst)	10 g
Toluhydroquinone (THQ; inhibitor)	0.10 g
Carbon black (specific surface area: 30 m^2/g; average particle size: 51 nm)	10.75 g
Chalk (for example GY 100)	1,183 g
Quartz sand (for example 16.14.2 quartz sand)	296 g

A bolting experiment is carried out as in Example 1 and, under the same conditions, a blocking time of 120 seconds is achieved.

Example 3

A sealing charge according to the invention, having the following composition, is prepared:

Unsaturated polyester resin	500 g (25%)
1,1-Di-tert.-butylcyclohexane peroxide (catalyst)	10 g
2,6-Di-tert.-butyl-para-cresol (for example, the product "Bisoxol"; inhibitor)	0.25 g
Carbon black (specific surface area: 30 m^2/g; average particle size: 51 nm)	10.75 g
Chalk (for example GY 100 chalk)	1,183 g
Quartz sand (for example 16.14.2 quartz sand)	296 g

A bolting experiment is carried out as in Examples 1 and 2 and, under the same conditions, a blocking time of 63 seconds is obtained.

If the three examples indicated above are compared with one another and with the comparison example using formulation 1 of our earlier Application, it is found, on the one hand, that the incorporation of carbon black makes it possible to achieve a better viscosity/reactivity compromise, and, on the other hand, that this carbon black does not detract from the intrinsic activity grading of the inhibitor with respect to temperature. In fact, it is seen that, when the 3,5-di-tert.-butyl-4-hydroxyanisole (which can be the product "Topanol 354" for example) of Example 1 is replaced by the toluhydroquinone of Example 2, whilst retaining the same amount of inhibitor, the blocking time is increased from 38 to 120 seconds, which completely represents the reactivity difference known to exist between the two products. Likewise, as regards the third inhibitor used, that is to say 2,6-di-tert.-butyl-para-cresol (which can be the product "Bisoxol" for example), it is seen that its lower activity leads to the use of a larger amount thereof, and this brings the blocking time down to 63 seconds.

Of course, it is possible to use products other than those given above as Examples.

Using formulation No. 2 of our Application No. 44234/78 (which contains approximately 19% of binder) under the conditions indicated above for the bolting experiment, the blocking time is 30 seconds.

A further comparison composition having the following formulation is prepared:

Matrix

Unsaturated polyester resin	: 17.29% of the final composition
1,1-Di-tert.-butylcyclohexane peroxide	: 2% of the resin
2,6-Di-tert.-butyl-para-cresol	: 0.1% of the resin.

Final composition

Matrix	: 18%
Chalk (GY 100)	: 65.6%
16.14.2 quartz sand	: 16.4%.

For a blocking experiment using a rod of diameter 18 mm and length 1 m, driven into a hole of diameter 22 mm with a rotation speed of 1,618 rpm, a blocking time of 39.5 seconds is obtained.

The above Examples and comparison examples show that the incorporation of carbon black makes it possible to achieve the desired compromise without detracting from the stability of the charge, which is surprising. Carbon black also exhibits additional advantages: its incorporation improves the quality of the seal by virtue of the resulting increase in the thermal conductivity; in fact, the seal very rapidly becomes more homogeneous. Carbon black has a high affinity for compounds which possess chromophoric groups and it consequently absorbs the excess of quinone or other stabiliser contained in the unsaturated polyester resin; this enables the organic peroxide to react more rapidly with the mixture of unsaturated

polyesters/styrene. Finally, carbon black acts as a reducing agent and this antioxidant function enables it to improve the storage stability of the mastics of the "single-component" type.

Carbon black also has a high specific surface area, which assists the absorption phenomena, and produces an additional effect of improving the viscosity when the mass is in movement.

Of course, depending on the batches of resin and the viscosity, it is possible to modify the solidification time outside the range disclosed in the non-limiting examples described above.

It is also possible to incorporate, into the matrix, a small amount of colloidal silica (for example at a rate of 2% of the resin) having a BET specific surface area of about 100 m^2/g, the function of which is to act as a suspending agent to prevent the products from separating out. However, this incorporation of silica is not essential.

Finally, it has been noted that the absence of inhibitor in the above charges containing carbon black results in a poor stability of the system; the presence of inhibitor is therefore necessary.

CLAIMS

1. A resinous composition comprising, as fillers, carbon black, 40 to 70% of chalk, and 10 to 40% of quartz sand, and sufficient of a resinous binder comprising unsaturated polyester resin, catalyst and inhibitor to form a matrix for the said fillers, the said percentages being by weight based on the weight of the composition.
2. A composition according to claim 1 in which the proportion of carbon black is 0.5 to 5% by weight of the unsaturated polyester resin.
3. A composition according to claim 2 in which the proportion of carbon black is about 2.15% by weight of the said resin.
4. A composition according to any one of claims 1 to 3 in which the carbon black has a specific surface area of 30 to 250 m^2/g. (BET).
5. A composition according to claim 4 in which the carbon black has a specific surface area of about 30 m^2/g.
6. A composition according to any one of claims 1 to 5 in which the average particles size of the carbon black is 13 to 51 nm.
7. A composition according to claim 6 in which the average particle size of the carbon black is about 51 nm.
8. A composition according to any one of claims 1 to 7, having a formulation in the following proportions:

Unsaturated polyester resin	500 g (25% by weight)
Catalyst	10 g
Inhibitor	0.10-0.25 g
Carbon black	10.75 g
Chalk	1,183 g
Quartz sand	296 g.

9. A composition according to any one of claims 1 to 8, in which the catalyst is 1,1-di-tert.-butylcyclohexane peroxide or tert.-butyl peroctoate, the inhibitor is 3,5-di-tert.-butyl-4-hydroxyanisole, toluhydroquinone or 2,6-di-tert.-butyl-para-cresol.
10. A composition according to any one of claims 1 to 9, containing colloidal silica as a suspending agent.
11. A composition according to claim 1 substantially as described in any one of Examples 1 to 3.
12. Process for positioning a strengthening rod in mine levels and other works which comprises introducing into a long bore made in a wall or other surface to be strengthened a composition as claimed in any one of claims 1 to 11 and a rod of substantially the same length as the bore and rotating the rod at a rotation speed which causes it to heat up by friction with the composition to the hardening temperature of the composition so as to cause the rod to be sealed in the bore by the hardening of the composition.
13. Process according to claim 12 in which the rod is rotated at a speed of between 500 and 3000 revolutions per minute.
14. Process according to claim 12 or 13 which comprises four successive stages, namely: a first stage in which the resinous composition is injected into the bore so as to fill 35% to 45% of the latter; a second stage, in which the rod which is to be sealed is introduced into the partially filled bore so that about 50% of its length is wetted by the resin; a third stage in which the rod is rotated at 800 to 2400 revolutions per minute for 15 to 60 seconds; and a fourth stage in which the rod is completely driven into the bottom of the hole while the rotation is continued until the resin has completely polymerized.

15. Process according to claim 12 substantially as hereinbefore described.

16. Walls and other surfaces of mine levels and other works when strengthened using the process of any of the preceding claims.

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